

Distinctive IR-Spectroscopic Features of Functional Groups of Low-Grade Phosphorites After Microbiological and Acid Processing

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Abstract

The article discusses the current problems of enrichment of low-grade phosphorites by the thermal method as well as the production of mineral fertilizers using various acids. An alternative biotechnological method for producing organomineral fertilizers using neutrophilic, heterotrophic microorganisms of activated sludge at a biochemical treatment station for municipal wastewater for the processing of low-grade phosphorites and the production of phosphorus-containing organomineral fertilizers is proposed. In this case, a natural acceleration of the processes of the phosphorus cycle in nature occurs, which does not pollute the environment. A comparative description of IR spectroscopic descriptions of the results of microbiological treatment and treatment with sulfuric and nitric acids showed distinctive characteristics of the appearance of functional groups, which showed the transfer of valuable phosphorus components during acid treatment to sediment and their irrevocable loss in the form of waste. The studies will serve the utilization of low-grade phosphorites unused in the production, the production of a new type of organomineral fertilizer using and recycling of human waste (in most countries, incinerated), will lead to a gradual improvement in the structural composition of soils. Human vital activity waste and low-grade phosphorites have zero cost, the applied technology of biochemical treatment of domestic wastewater is available in all major cities that can be used to enrich phosphorites with organic matter.

Keywords: activated sludge, microflora, microorganisms, neutrophils, heterotrophs, aeration tanks.

1. Introduction

Uzbekistan has created its own base of minerals resource for the production of phosphorus fertilizers. Phosphorite manifestations are found in many regions of Uzbekistan (Ferghana, Surkhandarya, Pritashkent, Navoi Central Kyzylkum, Bukhara-Khiva and Karakalpak) [1]. But the most promising, from the point of view of industrial development, turned out to be the Central Kyzyl Kum region [2].

The acid processing of phosphate feedstocks is the main way to produce phosphate fertilizers. Numerous methods have been proposed in the scientific literature for the enrichment of poor phosphorite ores with acids (HCl [3], H₂SO₄ [4,5], H₃PO₄ [6,7], HNO₃ [8,9]). Technological schemes for the production of complex fertilizers based on them have been developed. Strong acids actively dissolve carbonates, however, phosphates dissolve with them, which leads to a significant loss of P₂O₅.

Recently, man-made human impact has led to global pollution of the entire surface of the Earth. Therefore, the time has come for coordinated human interaction with the biosphere in the production of not only mineral fertilizers, but also other consumer products, taking into account environmental factors.

Our new method of biotechnological processing of phosphorites using microorganisms is based on the principle of modeling the evolutionary processes of the formation of mineral deposits and the ability of certain types of microorganisms in certain conditions to use mineral compounds as a power source. Many types of microorganisms that make up the microflora of activated sludge (AS) of a biological wastewater treatment plant, while in the wastewater, are able to absorb not only pollutants inside the cell, but also to destroy some insoluble minerals in

mineral deposits. They, acting on minerals with their intracellular and extracellular organic metabolites, subject them to biochemical transformations [10-12].

In literature [13], it is proposed to extract lipids from the composition of dehydrated solid runoff as biofuel. Sugars in acidic and neutral environments have a very low propensity for complexation with d-metals. In an alkaline environment, they form sugars, complexes of low stability and complex composition with a number of metals. Polysaccharides behave similarly to saccharides, which adsorb many metal ions and their salts due to physical and weak chemical coordination forces. The presence of two or more functional groups in hydroxy acids and amino acids ($-H$ and $-COOH$, $-NH_2$ and $-COOH$, etc.) promotes the growth of their complexing properties. The $-NH_2$ group - in amino acids, is a stronger electron pair donor than hydroxide- OH . The number of amino groups determines the higher strength of the complexes, while the number of carboxyl groups affects little. A strong tendency toward a decrease in the stability of the complexes during the transition from amino acids to peptides and polypeptides was observed, which is caused by a decrease in the number of strong electron-donating $-NH_2$ - and $-COO$ groups and the appearance of weak urea- $CONH$ groups. The AS ecosystem is artificially created and dependent on various environmental factors. Therefore, the species inhabiting it, in terms of number and species diversity, are significantly different from those that exist in the natural environment. Those microorganisms that began to dominate in numbers among the rest, due to natural selection associated with the characteristics of the composition and properties of the aeration tank nutrient medium created by wastewater, have high adaptive properties due to the conditions of their selective selection. In this biomass, colonies of bacteria and microorganisms are present, which ensure the release of carbon, biogenic and other elements from wastewater [13].

The evolutionary origin of mineral deposits is to some extent affected, not only by external environmental factors, but also by the close interaction of the living organic world with the inorganic one. In each AS, the active principle for the primary destruction of inorganic minerals is the isolation of microorganisms in the form of extracellular metabolites, enzymes that, together with the released cationic elements, form metal-organic complexes - chelates that can be easily absorbed by plants. For AS, regardless of the nature of industrial production or industry, the main mineral destructors are primarily heterotrophic bacteria, micromycetes and algae.

For this, the purpose of the research was a comparative IR spectroscopic study of the distinctive features of the emergence of new functional groups: a) after treatment of low-grade phosphorites with microflora of activated sludge at a biochemical treatment station, and b). treatment of phosphorites with concentrated sulfuric and nitric acids.

The research tasks included, simulating in laboratory conditions, the natural evolutionary processes of the phosphorus cycle in nature, to establish the mechanisms of destruction of calcite ($CaCO_3$) and francolite ($Ca_5(PO_4)_3(F,O)$) in phosphorites, as well as processes when treatment with acids can lead to positive results [14].

2. Method

The entity of the study was the low-grade phosphorite ore of the Central Kyzyl Kum from the Jeroy-Sardara deposit with the following complex chemical composition containing a high amount of carbonates (Table 1) [15]:

Table 1. Chemical composition of phosphorites of the Central Kyzylkum

No.	Compounds	Content of elements, (%)	No.	Compounds	Content of elements, (%)
1.	P_2O_5	8,0-12,0	8.	CO_2	8-15
2.	Al_2O_3	1,5-3,0	9.	F	1,8-3,2
3.	SiO_2	6,0-8,0	10.	SO_3	2,5- 3,5
4.	CaO	42-48,1	11.	U	0,003-0,008
5.	MgO	2,5-3,5	12.	REE amount	0,04-0,089
6.	Fe_2O_3	0,6-0,8	13.	H_2O	10,0
7.	R_2O	0.9-1.4	14.	Undissolved residue	8,0-8,2

To achieve the goal and objectives of scientific research, the following laboratory studies were performed at the Navoi State Mining Institute:

- studied the chemical and mineralogical composition of phosphorites and activated sludge;
- researches were carried out on leaching various elements from low-grade phosphorites of the Jeroy-Sardara deposit using aerobic types of neutrophilic, heterotrophic types of activated sludge microorganisms from the biochemical treatment station of NAVOIAZOT JSC;
- reactors simulating aeration tanks of biochemical treatment plants were created in which, at a ratio of S: L = 1: 4 (S-phosphorite, L-activated sludge) conducted destruction insoluble phosphorite compounds — calcite and francolite.
- used sulfuric (H_2SO_4) and nitric acids (HNO_3), which are used in the preparation of mineral fertilizers for comparative analysis;
- the study of the distinctive IR-spectroscopic features of functional groups in the composition of phosphorites were carried out before and after the experiment.

In production at the Kyzylkum phosphorite plant, the main enrichment method is the thermal method for getting rid of carbonates. We have chosen a softer and closer to natural conditions version of biotechnological leaching of carbonates using heterotrophic microorganisms. Microorganisms use carbonate carbon for their growth and development as a nutrient medium for the synthesis of the main biopolymers of the body - proteins, lipids and carbohydrates. The main phosphate mineral is francolite (fluorocarbonate apatite) and calcite compose phosphorites by 80-90% (Table 2), which also include carbonates. The microflora of activated sludge from aeration tanks from the biochemical treatment shop in the form of a liquid phase (L) was mixed with low-grade phosphorites and their waste by aeration in the form of sludge (S) in the ratio L: S = 4: 1.

Table 2. Average mineralogical composition of phosphorites of the Central Kyzyl Kum

Minerals	Chemical formula	Content%	Minerals	Chemical formula	Content%
Francolith	$Ca_5(PO_4,CO_3)_3(F,O)$	56,0	Gypsum	$Ca_2SO_4 \cdot 2H_2O$	3,5
Calcite	$CaCO_3$	22,5	Goethite	$Fe_2O_3 \cdot H_2O$	1,0
Fluorapatites,	$Ca_4(CaF)(PO_4)_3$		Zeolites		
Hydroxylapatites	$Ca_4(CaOH)(PO_4)_3$	4,0		Tetrahedral fragments of SiO_4 and AlO_4	less than 1.0
Quartz	SiO_2	7,5-8,0	Organic substance	Oxalates	About 0.5
Hydromica minerals and feldspars	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$ (Na, Ca, Ba)	4,0-4,5	Sum of Rare Elements	REE	0,03

The experiments were performed in several versions in reactors simulating aeration tanks using water, activated sludge, activated sludge with compressed air and continuous mixing.

After bacterial leaching for 14 days, the qualitative composition of the samples of the solid phase was analyzed on a SHIMADZU instrument (laboratory of the Novosibirsk State Hydrometeorological Institute, Department of Chemical Technology) of the IR-Fourier spectrometer IRTracer-100, by preparing compressed tablets in KBr. The absorption bands of infrared light correspond to antisymmetric wavelengths range from 400 to 4000 cm^{-1} .

3. Results

The results obtained by treatment with concentrated sulfuric and nitric acids showed a very crude and imperfect intervention in the composition of phosphorites with obtaining poor results of the release of EPA into the solution, as evidenced by the data on the study of the density of solutions (Table 4). The shape, volume and amount of precipitation in the IR spectra are spontaneously mixed with each other. For example, functional groups involving fluorine are noted both in solution and in sediment. Similar results were obtained with phosphorus, calcium and

magnesium. Uneven distribution of these elements occurs in solution and in sediment. In the production of mineral fertilizers, a lot of valuable components in waste are lost.

Table 3. shows that when studying the density of solid and liquid phases, the degree of density of microbiological treatment is superior to acid treatment, because natural interaction and fusion of organic and inorganic compounds occurs. The interaction with AI microflora also led to an increase in the density of the liquid phase, which means that not only anionic, but also cationic elements in the form of chelate complexes passed into the soluble fraction.

Table 3. The results of the hydrolysis of low-grade phosphorites during microbiological and acid treatment

Low grade phosphorites, 500 g	Microbiological treatment		H ₂ SO ₄ treatment		HNO ₃ treatment	
	Sludge density g/l	Density of the liquid phase, g/l	Sludge density g/l	Density of the liquid phase, g/l	Sludge density g/l	Density of the liquid phase, g/l
	1184,5	1087,6	1015,58	1030	360	1072

Chemical analysis of samples for the treatment of phosphorite and sludge with activated sludge showed the most optimal options in which the treatment of phosphorite and sludge was carried out in an aerated reactor plant simulating aeration tanks of a sewage treatment plant. The results are presented in table 4.

Table 4. Chemical composition and characteristics of promising options for the proposal of production

The chemical composition of the samples	The chemical composition of phosphate rock in the interaction of the liquid phase with a solid residue			The chemical composition of phosphorites in the treatment with concentrated acids.	
	FR+ H ₂ O	FR+AS (L.F.) + H ₂ O+O ₂	FR+AS (S.R) + H ₂ O+O ₂	H ₂ SO ₄ , 250 g/l	HNO ₃ , 250 g/l
Moisture	75,68	70,73	71,94	44	53
Organic matter	0,12	4,31	5,18	0,02	0,05
Ash	23,5	23,96	22,88	26,08	23,05
Nitrogen total (%)	0,03	0,12	0,14	0,02	3,13
P ₂ O ₅ total, %	3,54	3,58	3,76	2,16	2,46
P ₂ O ₅ digestible by Trilon B (%)	1,53	1,79	2,06	0,25	1,19
P ₂ O ₅ digestible/P ₂ O ₅ total, %	36,26	50,12	56,38	9,25	9,31
CaO _{total} , %	10,65	10,66	10,89	8,01	9,36
CaO _{digestible} by 2% citric acid. (%)	8,14	8,33	9,33	1,47	3,72
CaO _{digestible} / CaO _{total} , %	76,52	78,22	85,66	20,35	23,32
MgO	0,31	0,33	0,36	0,31	0,34
Dry weight	24,03	26,27	25,06	28,76	28,49

Analyses of the results of the chemical analysis of the selected above options were performed in the form in which they were in the reactors. The results are presented with the presence of high humidity, varying in the range of 70-75%. During acid treatment, due to the exothermic reaction, a certain amount of moisture evaporated and the humidity significantly decreased to 44-53%. The amount of organic matter, nitrogen, phosphorus, calcium and magnesium exceeds the amount in variants using a solid residue of AS and far exceeds the amount of these compounds in the liquid phase. However, the most interesting point in the use of the liquid phase of AS is manifested in the high activity of microorganisms, which consists in the fact that, compared with the control options, reliable results were obtained that could be obtained only under the influence of the biogenic factor. As a result of this, the transformation of mineral compounds in the composition of ore and sludge occurred, and the main macroelement compounds from the insoluble form turned into the soluble one.

4. Discussion

Activated sludge is a complex substance, which is microflora involved in the wastewater treatment process and is an amphoteric colloidal system. Organic substances active sludge contain 70-90% of organic substances in living organisms. They are represented by 12 main types of simple microorganisms. The main activators of sludge are bacteria. 1m³ contains up to $2 \cdot 10^{14}$ [13]. They form clusters surrounded by mucus. Numerous species of protozoa and microorganisms live in the sludge biocenosis, capable of transforming phosphate compounds of detergents, cellulose and various human excretions that enter the municipal wastewater.

In an artificial form, the trophic pyramid of the food chain was formed in the microflora of AS, consisting of protozoa that feed on bacteria and various heterotrophic types of bacteria that feed on cellulose, protein, lipid and other components of domestic wastewater. The simplest microorganisms in the form of rotifers, amoeba and ciliates serve as indicators of the number of bacteria. The more protozoa, the more active the microflora of AS. During the processing of every 1000 m³ of wastewater, 250-300 liters of dehydrated sludge with 80% moisture are formed. The total lipid content in activated sludge ranges from 24.0-36.8% by weight. Up to 16 fatty acids are found in the composition of lipids [13].

Analyses of the chemical composition of activated sludge and samples of activated sludge with phosphorites were carried out at the Research Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan (Table 5) using the main methods of M. Zharsky. and M.M. Vinnik, adopted in inorganic chemistry [16 - 17].

Table 5. Chemical composition of activated sludge from workshop No. 56, biochemical treatment station of Navoiyazot JSC

The composition of activated sludge,%								
Water	Organic matter	Nitrogen	P ₂ O ₅	K ₂ O	CaO	MgO	ash	dry weight
95,38	2,99	0,12	0,14	0,01	0,17	0,02	1,41	4,67
Calculated in dry matter,%								
10,05	28,54	11,44	13,35	0,95	16,21	1,90	13,44	44,26

From table 5, it can be seen that the composition of AS is rich in basic macroelements - nitrogen, phosphorus, potassium, calcium and magnesium oxides, which are necessary for the growth and development of plants. Therefore, AS from a biochemical treatment plant for sewage and municipal waste after some refinement, in itself, can serve not only as a ready-made organic fertilizer, but also as a factor where the microflora of AS can actively influence, transform and degrade insoluble mineral compounds in the composition of phosphorites.

To detect various types of functional deviations in the composition of phosphorites and AS when deciphering the peaks of the IR spectra, we used a monograph by K. Nakamoto et al. [18] and based on them a summary table of the detected functional groups was obtained. IR spectroscopic study of various types of interaction of microflora of activated sludge with phosphorites, the features of various functional mobile groups of nitrogen, potassium, phosphate and calcium can help to get an idea about the chemical structural composition of a new species obtained organic fertilizer. Figure 1 shows the IR spectrum of activated sludge, where the concentration of humic compounds is distributed over the entire length of the spectrum and covers wavelengths from 500 to 4000 cm⁻¹. Protein fractions are distributed in the range of wavelengths spanning the spectrum around the length from 2 to 300 cm⁻¹. Phosphorus compounds in the form of P-O, P=O, P=S, P-O-P, O-P-O bonds are in the wavelength

ranges from 500 to 1000 cm^{-1} . Functional nitrogen compounds are distributed in the form of KNO_3 and are in the spectrum of 1000 cm^{-1} , and the ammonium, amine and ammonia bonds cover the vibrational range from 2400 to 3500 cm^{-1} . Potassium compounds are expressed as KNO_3 and KOH bonds, the first is in the range of 1000, 1600 cm^{-1} , and KOH is in the band of 3600 cm^{-1} . Detected macronutrients are distributed over a very wide range of variation and appear to be part of aromatic compounds.

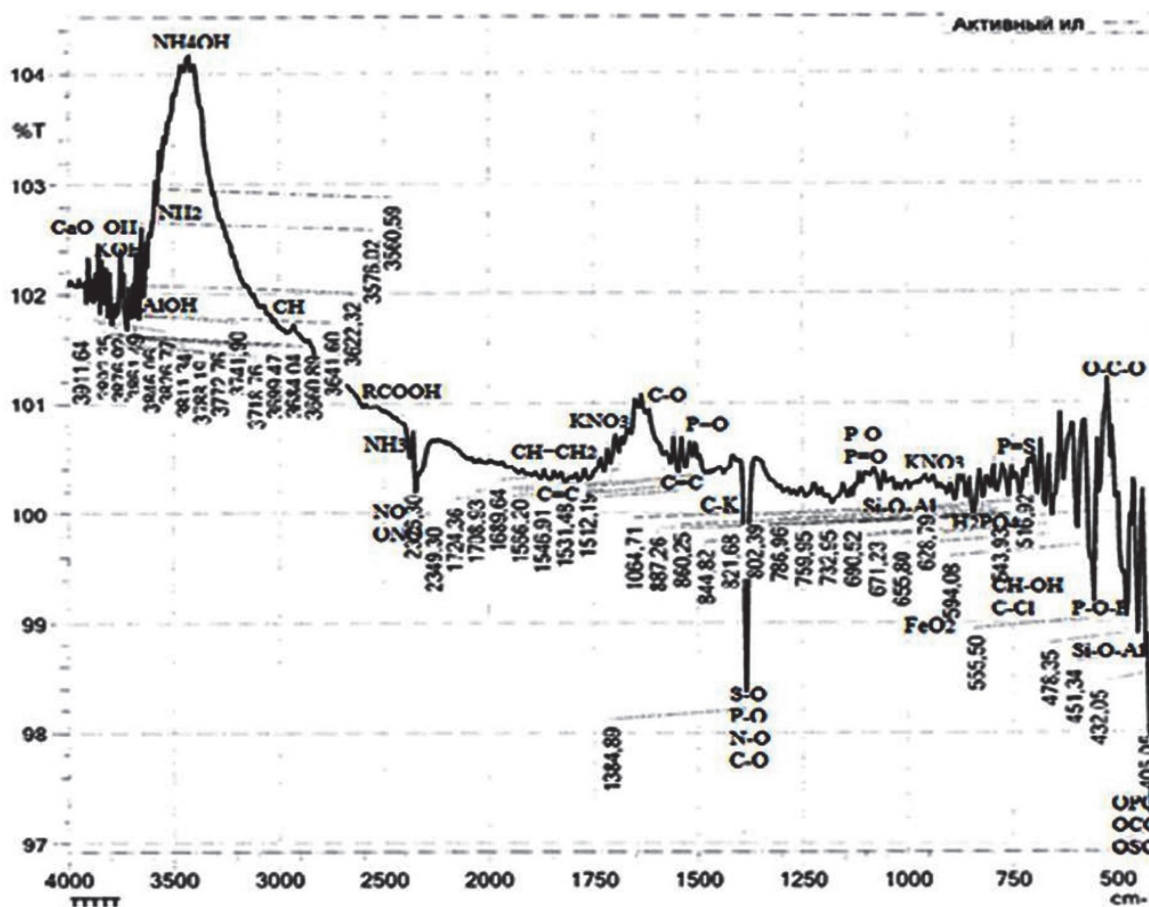


Figure 1. Functional groups of the IR spectrum of activated sludge

A more interesting picture and a wide range of wavelength variation in the distribution of functional groups were shown by the IR spectra of low-grade phosphorites (Figure 2), where francolite spectra were clearly identified, covering wavelengths from 995 to 1600 cm^{-1} . The degree of density and permeability of the francolite mineral by infrared rays was very large and ranged from 0 to 8%. Calcium compounds in the form of calcite mineral were not only part of francolite, but they were also distributed in the form of free calcite (CaCO_3) and CaO over wavelengths from 800 to 3800 cm^{-1} .

The analysis of infrared absorption spectra showed the following types of bonds: P-O-C, P=O, P-O-P, P-O-Al, bands 1200-900 cm^{-1} , P-F bands 900-800 cm^{-1} , P-C bands 720-680 cm^{-1} , P-Cl, P=O-S bands 520-460 cm^{-1} , PO_4^{3-} bands 1100-100 cm^{-1} , Si-O-Si bands 1090-1020 cm^{-1} , CO_3^{2-} 1450-1410 cm^{-1} . It follows that the composition of phosphorite is actually very complex and includes aluminosilicate minerals - merwinite and forsterite (bands 460-466 cm^{-1}), quartz (bands -1085-2090 cm^{-1}), phosphosiderite (bands 790-797 cm^{-1}). The replacement of the PO_4^{3-} ion in the fluoroapatite molecule by the CO_3^{2-} group can probably be judged by the shift of the maxima of the PO_4^{3-} vibrational band to the high-frequency region due to the overlap of the carbonate absorption band in the phosphate mineral.

Thus, in the IR spectra, we were able to determine the location of the main phosphorite mineral - francolite in the composition of phosphate rock, which is in the wavelength range from 800 to 1800 cm^{-1} .

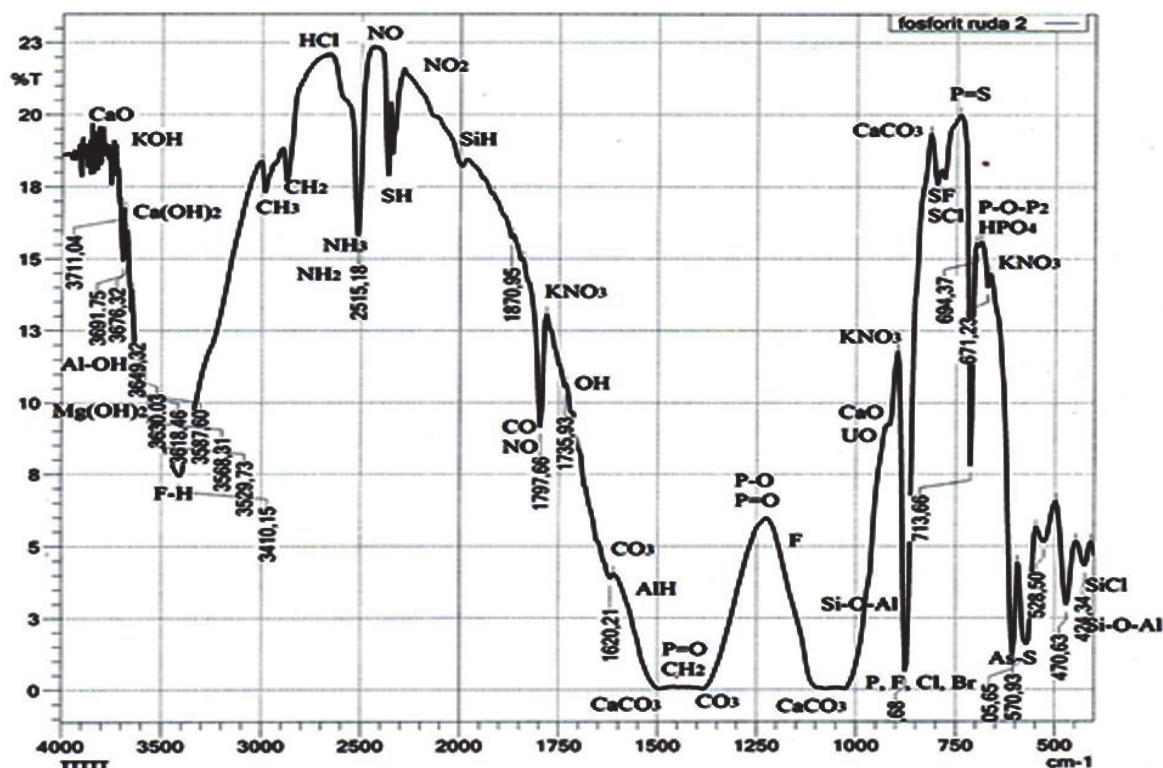


Figure 2. Functional groups of the IR spectrum of phosphate rock

When phosphorite ore and sludge was added to the composition of activated sludge (AS) in the ratio T: W = 1: 4 during intensive aeration, the organic matter of activated sludge was actively mixed with inorganic compounds of phosphorites, which led to a sharp change in the peaks of the IR spectra in Figure 2. The main absorption bands of infrared radiation were already in the range from 3650 cm^{-1} to 3950 cm^{-1} , which corresponds to such functional groups as CaCO_3 , CaO , Ca(OH)_2 , $-\text{O-N}$, COO-H , X-H - those vibrations involving hydrogen atoms. It has been established that the absorption bands of the infrared rays of the samples under active exposure to air are practically the same, which indicates the important role of oxygen introduced into the aeration tank. Microflora AS in interaction with phosphorite caused a transition to an unstable state of many groups of elements. Calcite CaCO_3 was found in a wide variety of compounds, turning into the following functional groups of elements — CaO , Ca(OH)_2 , $\text{CaSO}_4 \cdot \text{H}_2\text{O}$. Groups of alkaline earth elements turned into weak bases - NaOH and KOH . Chlorine ions turned into weak solutions of HCl , HOCl , $[\text{ClO}_3]^-$ and formed complexes in the form of $[\text{CuCl}_4]^-$. Phosphorus compounds underwent a significant change, which turned into the following functional groups - $[\text{PO}_4]^{3-}$, P-OH , P=S , P-O , P=O , O-P-O , PO_4 , HPO_4 , H_2PO_4 . The nitrogen element in the composition of AS underwent insignificant changes and formed the following functional groups - KNO_3 , NH_4NO_3 , HNO_3 , NH_3 , RCOOH . The last compound - NH_3 , RCOOH can be classified as amino acids in proteins.

In contrast to the control option, the spectrum of the appeared groups of functional compounds increased several times, and if in the control variant there were 12 compounds, then in the variant with aeration 33 groups of functional compounds appeared. If in the IR spectrum of AS the degree of absorption of infrared rays reached from 97 to 104%, and in phosphate rock the degree of absorption of infrared rays was from 0 to 14%, which indicates a low permeability of the mineral, inorganic mass. After exposure to phosphorites by microflora AS, a different picture was observed, where the entire mass of phosphorites acquired a finer and more permeable structure. As a result, the degree of absorption of infrared rays in phosphorites after exposure to AS was high and reached 175-225%.

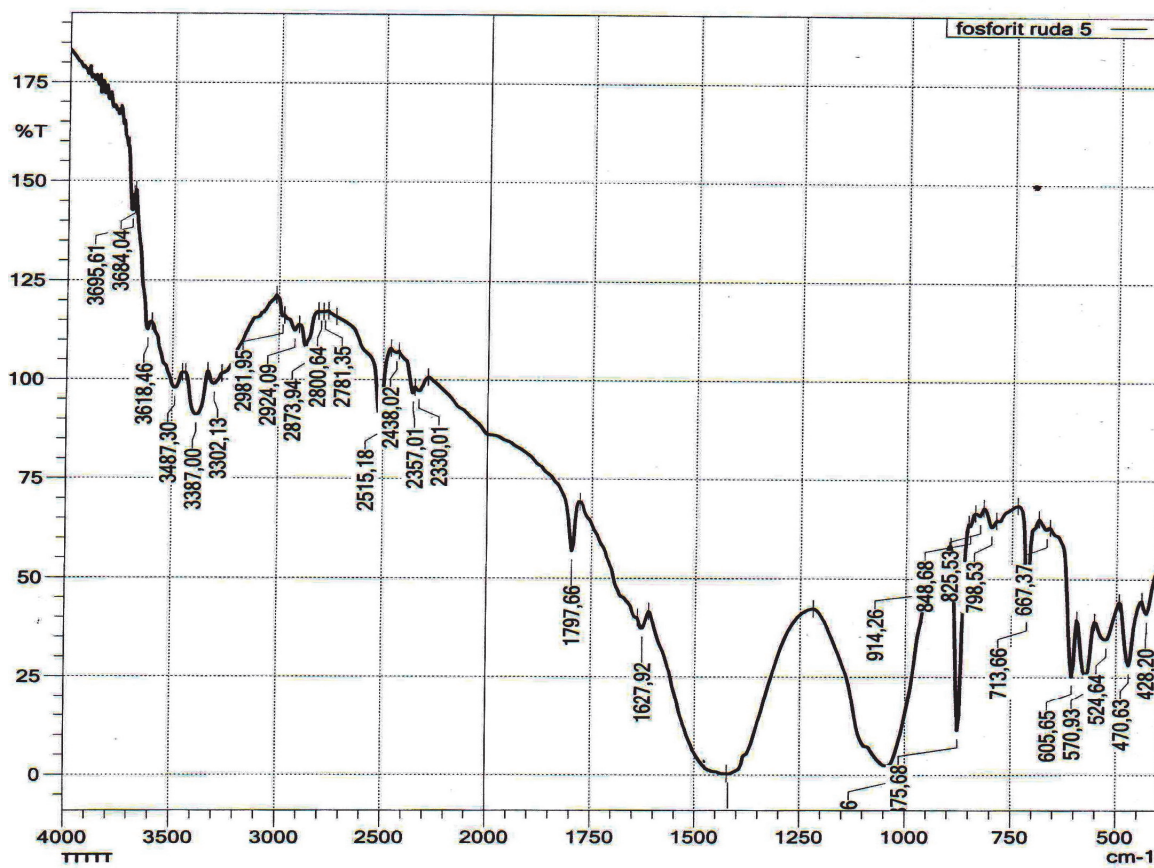


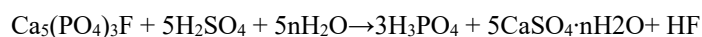
Figure 3. IR spectra of phosphorite ore activated sludge treatment options

On microscopic examination of the samples, the uneven, trapezoidal grains of francolite were rounded and became very small. Under a microscope, calcite, in the form of marble blocks, was practically crushed and turned into small crumbs. The IR spectrum peaks corresponded to the functional groups CaCO_3 , $\text{CaSO}_4 \cdot \text{H}_2\text{O}$, PO_4 , HPO_4 , H_2PO_4 , $\text{P}=\text{O}$, PO , CH_2 , CH_3C , $(\text{CH}_3)_2\text{C}$, $(\text{CH}_3)_3\text{C}$, $[\text{SO}_3]^{2-}$, HNO_3 , KNO_3 , which means that functional groups of minerals are found in compounds of various types of cyclic aromatic compounds, most likely humic acids.

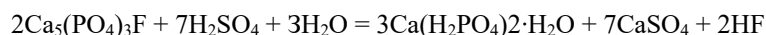
Conclusions based on the analysis of the characteristic lines of the IR spectrum confirm the data on the elemental composition of active sludges containing impurities of low molecular weight substances and humic acids. Given the high nitrogen content and atomic ratios of H/C, O/C, N/C, we can say that activated sludge is enriched in aliphatic and amine-containing functional groups.

A comparative characteristic of the absorption bands between phosphorite ores and AS showed that microorganisms actively interact not only with organic matter, but also with inorganic components of phosphorites, which is confirmed by diagrams of IR spectra.

When treated with sulfuric acid, the main reaction products of the stoichiometric amount of sulfuric acid and phosphorites were calcium sulfate and phosphoric acid. In practice, sulfuric acid processing of phosphorites with concentrated sulfuric acid is used at a stoichiometric ratio with phosphorite. As a result, superphosphate, double superphosphate are obtained as the final product, and extraction phosphoric acid (EPA) can be isolated. As a result, francolite breaks down to form phosphoric acid:



Upon generation of superphosphate, the following reaction occurs:



In fact, IR spectroscopic investigation showed that this does not happen, because part of phosphorus, calcium, magnesium and fluorides remains in the sediment and is lost in waste. In addition, during acid treatment, an exothermic reaction occurs, in which the solution boils with the release of copious foam. Then the solution quickly

thickens and turns into a dense pasty mass. Subsequently, when separating the solution into solid and liquid parts, filtering is very slow and difficult. Despite the prevalence of the sulfuric acid extraction method in the industrial production of phosphate fertilizers, the latter has a number of disadvantages, in particular, the formation of large amounts of waste in the form of phosphogypsum. In addition, an excess $\text{CaO}/\text{P}_2\text{O}_5$ ratio compared with phosphorite requires a large expenditure of acid for decomposition and leads to the release of a greater amount of phosphogypsum [19].

Figure 4 shows that in the francolith, which consists mainly of two large wide peaks, only one peak was split, corresponding to a wavelength of 1500 to 1900 cm^{-1} . The second peak at wavelengths from 100 to 1400 cm^{-1} remained untouched. In addition, at wavelengths from 3000 to 3700 cm^{-1} , a broad peak appeared in the form of an insoluble mineral compound - phosphogypsum ($\text{CaSO}_4 \cdot 7\text{H}_2\text{O}$), fluorides and various hydroxides. The permeability of infrared rays dropped to zero, which indicates the difficulty of processing the precipitate that appears, which contains some of the phosphorus.

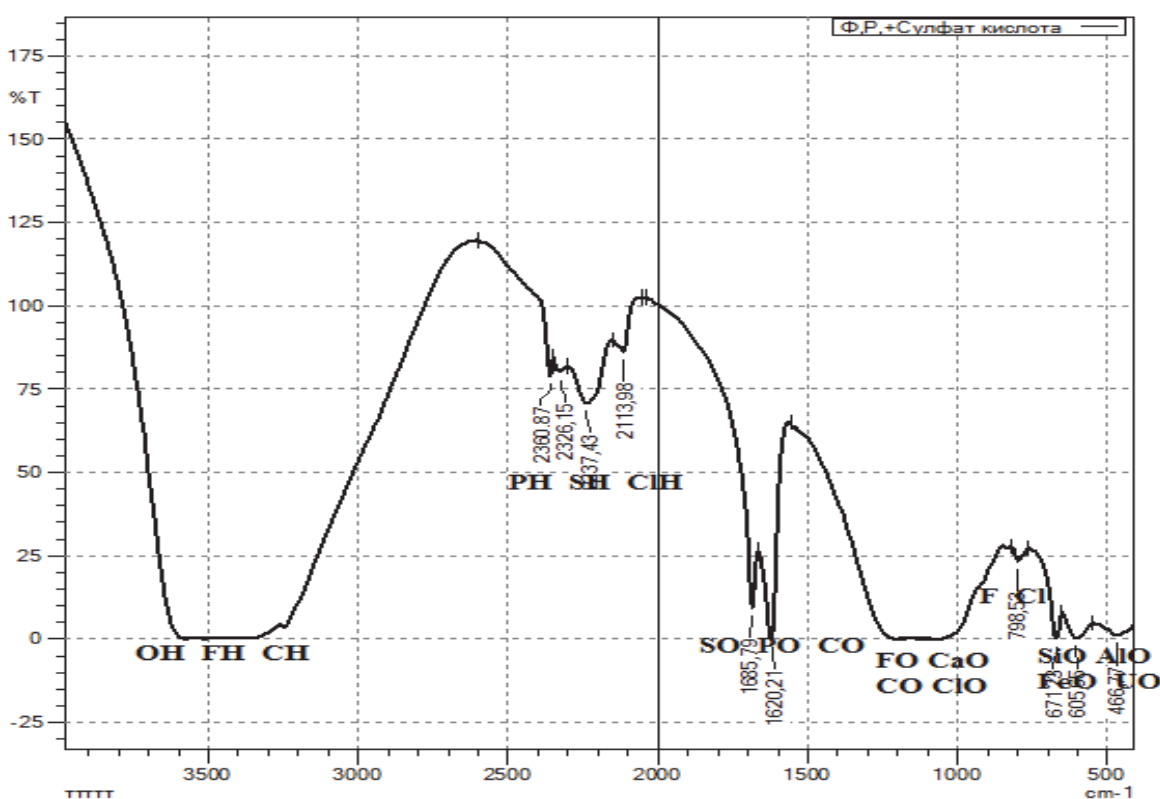
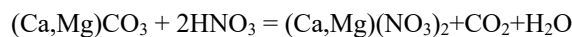
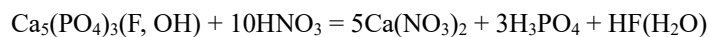


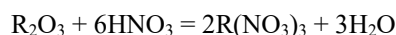
Figure 4. IR spectroscopic characterization of phosphorites treated with sulfuric acid

Treatment with nitric acid (HNO_3) led to the complete preservation of francolite, corresponding to wavelengths from 800 to 1800 cm^{-1} , with the appearance of wide peaks only in the wavelength range corresponding to 3200-3700 cm^{-1} , where insoluble compounds with functional groups of fluorine and nitrogen.

The chemistry of the processes of nitric acid opening of phosphorites is quite complicated due to the multicomponent nature of the system. During the process, the main chemical reactions take place:

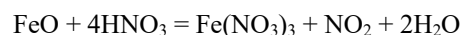


Sesquioxide and iron oxide (II) nitrate decomposed to form:



where R is Fe, Al

The phosphates of aluminum and iron formed during the reaction are poorly soluble in water and poorly absorbed by plants. In this case, alumina is a less harmful impurity. Iron (II) oxide decomposes with the release of nitrogen dioxide:



In addition to iron (II) oxide, the sources of nitric oxides are organic impurities that reduce nitric acid, as well as technical nitric acid itself, which contains a certain amount of nitrogen dioxide [19].

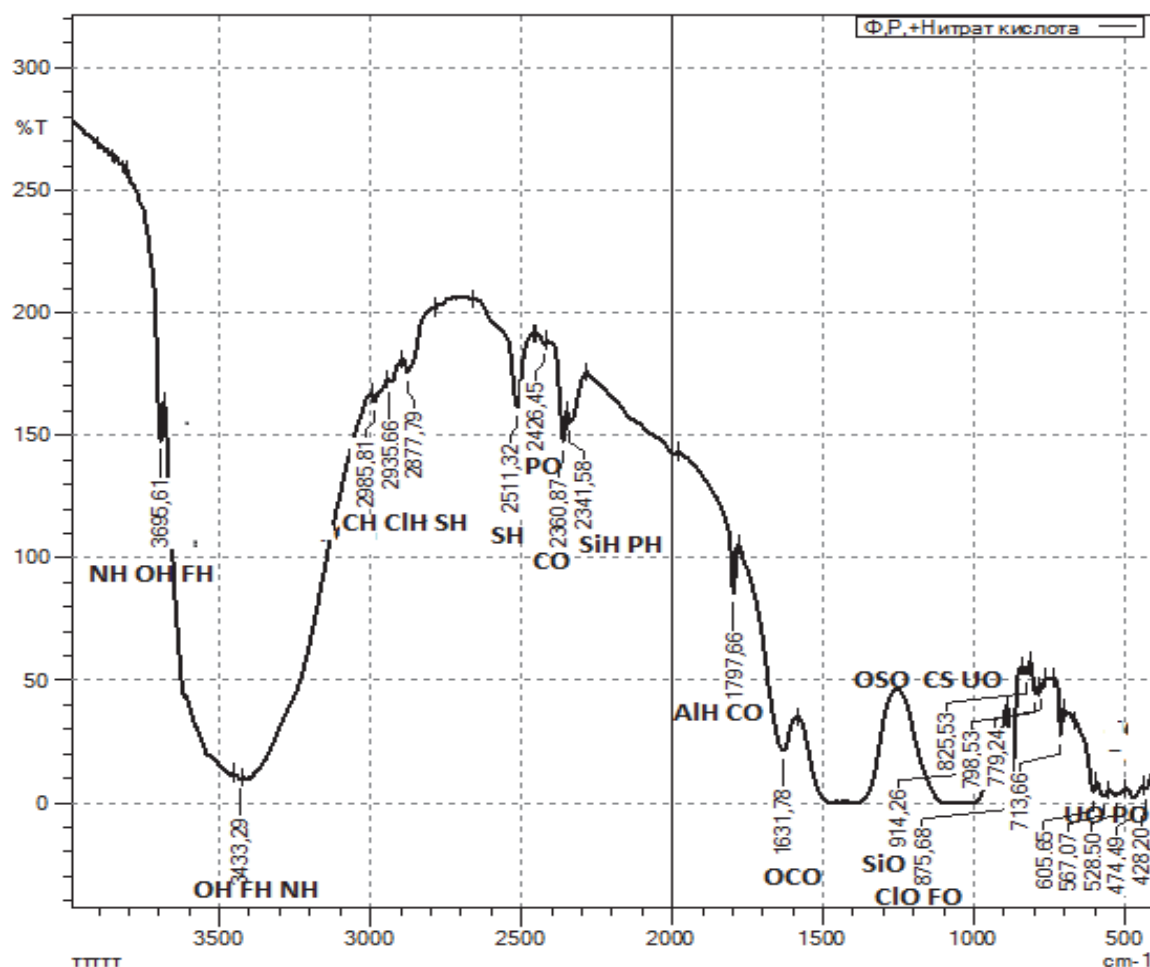


Figure 5. IR spectroscopic characterization of phosphorites treated with nitric acid

5. Conclusion

With the intensification of the processes of interaction of AS microflora with low-grade phosphorites and their waste in the form of sludge, a natural organic fusion of microflora and organic sediment of AS with phosphorites is noted. In parallel with this, the reverse process of the phosphorus cycle in nature was intensified, which caused the process of the transition of the unassimilable form of phosphorite to the assimilable one. The interaction of humic acids with silicates and aluminosilicates in phosphorites occurred due to the connection of carboxyls of humic substances with OH groups of inorganic compounds. Nitrogen-containing groups of organic molecules can also take part in the formation of bonds between organic and inorganic substances.

The analysis of the IR spectra of activated sludge variants showed an active interaction of AS microflora with phosphorite ore, where a shift of bands in the region of high or low frequency spectra was noted. Francolite, covering wavelengths from 800 to 1800 cm^{-1} , after exposure to microorganisms AS becomes less dense and decreases in size, and the bandwidth is somewhat narrowed. This circumstance emphasizes the active influence of AS microorganisms on the composition of francolite, where francolite, which manifests itself in the form of microscopically uneven brown phosphorite grains, becomes smaller, and phosphorus compounds and other elements become soluble. The new functional groups that appeared under the influence of microorganisms with oscillating spectra of molecules, in turn, are very active, since there is a change in the valency of molecules that cannot exist in a stable state and therefore they are combined with other functional groups, which leads to the formation of a new mineral formation and chelating compounds. The acid treatment of phosphorites has led to a

rough distribution of valuable components in the solution and sediment, which leads to low quality of the resulting mineral fertilizers.

Thus, the study of the IR spectra of AS, phosphorite ore in various variations with AS allowed us to establish the possibility of accelerating the natural mechanisms of the phosphorus cycle in nature with the prospect of obtaining a qualitatively new organomineral fertilizer, as well as the selection of a special technological scheme for processing low-grade phosphorite ore. An analysis of the IR spectra also revealed the presence of granular francolite, which, under the influence of microflora AS, became more loose due to the separation of calcite from its composition.

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